PHYS393 – Statistical Physics

Part 3: The Maxwell-Boltzmann Gas

The Boltzmann distribution

In the previous parts of this course, we derived the Boltzmann distribution:

$$n_j = \frac{N}{Z} e^{-\frac{\varepsilon_j}{kT}}, \tag{1}$$

We applied this distribution to two example systems: a spin-$\frac{1}{2}$ magnetic solid, and a collection of 1-dimensional quantum harmonic oscillators. We saw how to derive a number of properties of these systems, including the energy, heat capacity, and entropy as functions of temperature.

The partition function Z plays an important role in calculating quantities such as the total energy and entropy. It is defined by:

$$Z = \sum_j e^{-\frac{\varepsilon_j}{kT}}. \tag{2}$$

In this part of the lecture course, we shall apply the ideas and methods we have learned to a further system: the Maxwell-Boltzmann gas. This provides a simple model of a gas, that describes some important properties of gases quite well in a number of cases.

Discussing this example will also reinforce some the ideas and methods we have learned so far.

The most important new concept is that of the *density of states*. This is introduced because the energy levels in this system have a more complicated structure than in the previous two examples. We need to make some approximations to be able to evaluate the partition function and other important quantities.

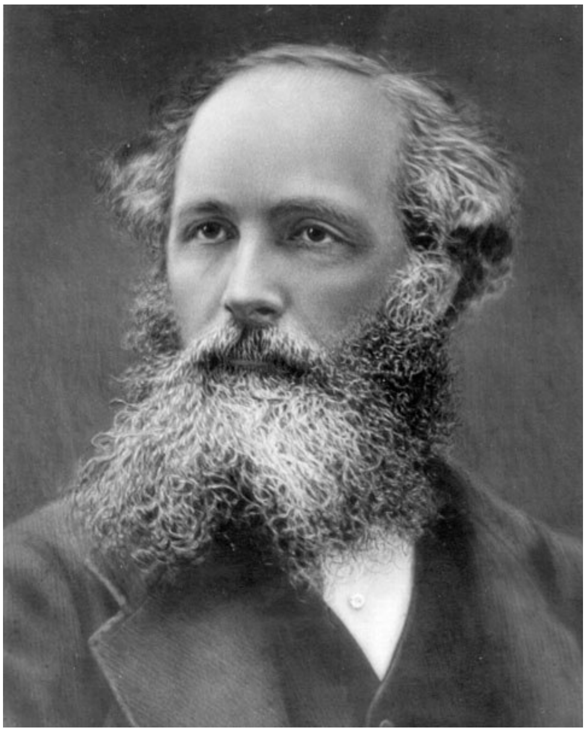
Consider a gas in a box of fixed volume. The gas consists of particles that are free to move within the box, but cannot penetrate the walls. We will assume that the density is low, so that collisions between gas particles are infrequent: this satisfies the condition that particles in the system interact only weakly with each other.

Our goal, as in the previous examples, is to find quantities such as energy, heat capacity and entropy as functions of temperature. In principle, we use the same equations and techniques for this system as for the previous two examples. However, we first need to do some work to identify the energy levels.

We shall use a quantum model for the gas particles: this will ensure that the allowed energy levels within the box occur at discrete intervals.

Our system consists of a low-density gas of particles, which move freely apart from occasional collisions with the (rigid) walls or with each other. To distinguish this gas from others that we will consider later, we refer to the system as a *Maxwell-Boltzmann* gas.

A further assumption we will make, at least for the time being, is that the gas particles have no internal structure. This means that there is no energy associated with rotations or internal vibrations of the particles. In practice, such a situation is closely approximated if the gas particles consist of single atoms – as in the case of noble gases (helium, neon...)



For simplicity, consider a square box of side length L. The wave function $\psi(x, y, z)$ of a particle in the box must satisfy the boundary conditions:

$$\psi(x, y, z) = 0 \quad \text{for} \quad x = 0, \text{ or } y = 0, \text{ or } z = 0, \tag{3}$$

and:

$$\psi(x, y, z) = 0 \quad \text{for} \quad x = L, \text{ or } y = L, \text{ or } z = L. \tag{4}$$

The boundary conditions are satisfied by a wave function of the form:

$$\psi(x, y, z) = A \sin(k_x x) \sin(k_y y) \sin(k_z z), \tag{5}$$

if:

$$k_x = \frac{\pi n_x}{L}, \quad k_y = \frac{\pi n_y}{L}, \quad k_z = \frac{\pi n_z}{L}, \tag{6}$$

where n_x, n_y, and n_z are positive integers.

The wave function (5) is an energy eigenfunction, since it solves the time-independent Schrödinger equation:

$$\hat{H}\psi = \varepsilon\psi, \tag{7}$$

where $\hat{H}$ is the Hamiltonian operator:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 \tag{8}$$

and ε is a constant, the energy of the particle. Substituting from (5), we find:

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}\left(n_x^2 + n_y^2 + n_z^2\right)\psi. \tag{9}$$

Hence, the energy levels are given by:

$$\varepsilon = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}\left(n_x^2 + n_y^2 + n_z^2\right) = k\theta\left(n_x^2 + n_y^2 + n_z^2\right). \tag{10}$$

The parameter θ (with units of temperature) is defined:

$$\theta = \frac{\hbar^2\pi^2}{2mkL^2}. \tag{11}$$

We now run into trouble. If we want to evaluate populations, total energy, heat capacity etc. as functions of temperature, the next step is to evaluate the partition function:

$$Z = \sum_j e^{-\frac{\varepsilon_j}{kT}}. \tag{12}$$

Here, the index j will actually be a triple index, for n_x, n_y and n_z. But quite apart from that, the summation is now difficult to evaluate.

To make things more convenient, we shall assume that we can replace the summation by an integral, and write:

$$Z = \sum_j e^{-\frac{\varepsilon_j}{kT}} \to \int_0^\infty g(\varepsilon) e^{-\frac{\varepsilon}{kT}} \, d\varepsilon. \tag{13}$$

Here, $g(\varepsilon)$ is the *density of states*: the number of energy states in the (small) energy range ε to $\varepsilon + d\varepsilon$ is $g(\varepsilon)d\varepsilon$.

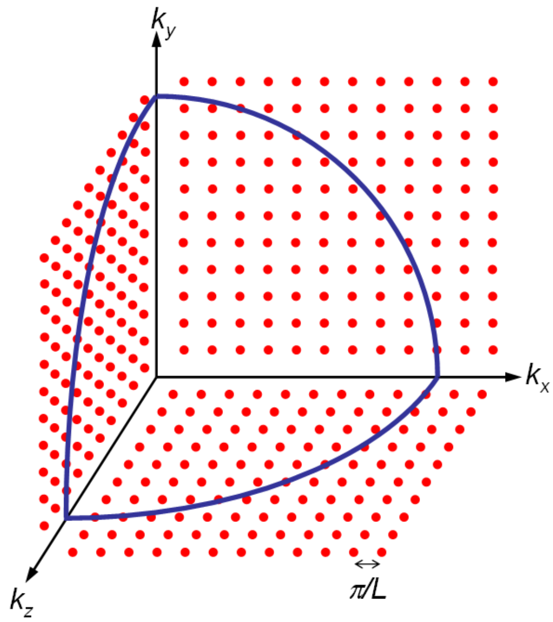
To evaluate the partition function, we need an expression for the density of states, $g(\varepsilon)$. As an intermediate step, we will find the density of states in k-space, $g(k)$, and then convert to the density of states as a function of energy.

In k-space, states lie on a 3-dimensional rectangular grid of points with spacing π/L between points.

The number of points in the region bounded by k and $k + dk$ is:

$$g(k)\, dk \approx \frac{4\pi k^2 dk}{8} \times \frac{1}{(\pi/L)^3}. \tag{14}$$

The first factor is the volume between spherical shells of radius k and $k + dk$, and the second factor is the number of grid points per unit volume of k-space. The approximation is valid for large k, i.e. at high energies.



$$g(k)\,dk \approx \frac{4\pi k^2 dk}{8} \times \frac{1}{(\pi/L)^3} \quad \text{(for large k).}$$

With the assumption of large k, we have:

$$g(k)\,dk = \frac{4\pi k^2}{8(\pi/L)^3}\,dk, \tag{15}$$

and:

$$\varepsilon = \frac{\hbar^2 k^2}{2m}. \tag{16}$$

Hence:

$$g(k)\,dk = \frac{4\pi}{8(\pi/L)^3}\frac{2m\varepsilon}{\hbar^2}\frac{dk}{d\varepsilon}d\varepsilon. \tag{17}$$

Also, from equation (16), we have:

$$k = \sqrt{\frac{2m\varepsilon}{\hbar^2}} \qquad \therefore \qquad \frac{dk}{d\varepsilon} = \frac{1}{2}\sqrt{\frac{2m}{\hbar^2\varepsilon}}. \tag{18}$$

So, writing $V = L^3$, we have for the density of states:

$$g(\varepsilon)\,d\varepsilon = \frac{4\pi}{8(\pi/L)^3}\frac{2m\varepsilon}{\hbar^2}\frac{1}{2}\sqrt{\frac{2m}{\hbar^2\varepsilon}}d\varepsilon = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{\varepsilon}\,d\varepsilon. \tag{19}$$

Maxwell-Boltzmann gas: partition function

In terms of the parameter θ (11), the density of states can be written:

$$g(\varepsilon)\, d\varepsilon = \frac{\pi}{4}\sqrt{\frac{\varepsilon}{(k\theta)^3}}\, d\varepsilon, \tag{20}$$

we can evaluate the partition function (13):

$$Z = \int_0^\infty g(\varepsilon) e^{-\frac{\varepsilon}{kT}}\, d\varepsilon. \tag{21}$$

Substituting for $g(\varepsilon)\, d\varepsilon$ from (20) into (21) gives:

$$Z = \frac{\pi}{4}\frac{1}{(k\theta)^{\frac{3}{2}}}\int_0^\infty \sqrt{\varepsilon}\, e^{-\frac{\varepsilon}{kT}}\, d\varepsilon. \tag{22}$$

The result of the integral is:

$$\int_0^\infty \sqrt{\varepsilon}\, e^{-\frac{\varepsilon}{kT}}\, d\varepsilon = \frac{\sqrt{\pi}}{2}(kT)^{\frac{3}{2}}. \tag{23}$$

So the partition function becomes, for high temperature:

$$Z = \left(\frac{\pi}{4}\frac{T}{\theta}\right)^{\frac{3}{2}}. \tag{24}$$

Maxwell-Boltzmann gas: low density approximation

So far we have assumed that the gas is of low enough density that particles interact only occasionally. In a classical model, this simply means that the total volume occupied by the particles is much less than the total volume of the container.

However, we are using a quantum model. In quantum mechanics, the strength of the interaction between two particles depends on how much their wave functions overlap. Two particles in states with similar wave functions will interact more strongly than the same particles in states with very different wave functions.

Therefore, to validate our assumption of weak interactions, we need to check that the mean occupancy of any state in the system is low.

In the Boltzmann distribution, the number of particles in a state with a particular energy ε_j is:

$$n_j = \frac{N}{Z} e^{-\frac{\varepsilon_j}{kT}}. \tag{25}$$

Since the exponential factor can have a value up to 1, the occupancy of any state will be small if:

$$\frac{N}{Z} \ll 1. \tag{26}$$

This is the condition that must be satisfied for our assumption of low density, and therefore infrequent collisions between particles, is to be satisfied.

Using equation (24) for the partition function, we can write:

$$\frac{N}{Z} = N \left(\frac{4}{\pi} \frac{\theta}{T} \right)^{\frac{3}{2}} = \frac{N}{V} \left(\frac{2\pi \hbar^2}{mkT} \right)^{\frac{3}{2}}. \tag{27}$$

Let us consider the case of (monatomic) helium gas, at s.t.p. One mole of an ideal gas at s.t.p. occupies 22.4 litres. Therefore, we use the following values:

$$\begin{aligned} N &= 6.02 \times 10^{23}, \\ V &= 22.4 \times 10^{-3} \text{ m}^3, \\ \hbar &= 1.05 \times 10^{-34} \text{ Js}, \\ m &= 6.69 \times 10^{-27} \text{ g}, \\ k &= 1.38 \times 10^{-23} \text{ J/K}, \\ T &= 273 \text{ K}. \end{aligned}$$

With these values, we find $N/Z \approx 3.9 \times 10^{-6}$: the low density condition is satisfied.

Maxwell-Boltzmann gas: low density approximation

Let us consider the worst case: helium gas at 1 atm pressure and 5 K (the boiling point is 4.2 K). In this case, the volume (assuming ideal gas behaviour) is:

$$V' \approx \frac{T'}{T} V = \frac{5}{273} \times 22.4 \text{ dm}^3. \tag{28}$$

With the new values:

$$\begin{aligned} V &= 0.410 \times 10^{-3} \text{ m}^3, \\ T &= 5 \text{ K}. \end{aligned}$$

we find:

$$\frac{N}{Z} \approx 0.085. \tag{29}$$

This is now getting somewhat close to 1: the Maxwell-Boltzmann theory should still give a reasonable description of the behaviour of helium at 5 K, but we should also not be surprised if the predictions of the model are not terribly accurate.

Maxwell-Boltzmann gas: total energy (1)

Now that we have the partition function Z (for high temperature), we can calculate the total energy from:

$$U = N \frac{d \ln(Z)}{d\beta}, \tag{30}$$

where $\beta = -1/kT$. Writing the partition function in the form:

$$Z = \left(-\frac{\pi}{4} \frac{1}{k\beta\theta} \right)^{\frac{3}{2}}, \tag{31}$$

we find:

$$\ln(Z) = \frac{3}{2} \ln \left(-\frac{\pi}{4} \frac{1}{k\beta\theta} \right). \tag{32}$$

Differentiating with respect to β gives:

$$U = N \frac{d \ln(Z)}{d\beta} = -\frac{3}{2} \frac{N}{\beta}. \tag{33}$$

The result, valid in the high temperature (classical) limit, is:

$$U = \frac{3}{2} NkT. \tag{34}$$

Of course, we should also be able to calculate the total energy by summing the energies of the various states, weighted by the population determined from the Boltzmann distribution.

The number of states within the energy range ε to $\varepsilon + d\varepsilon$ is $g(\varepsilon)d\varepsilon$. The number of particles within each of these states is:

$$n(\varepsilon) = \frac{N}{Z} e^{-\frac{\varepsilon}{kT}}, \tag{35}$$

and these particles have energy ε. Hence, the total energy of the system is:

$$U = \frac{N}{Z} \int_0^\infty g(\varepsilon) \varepsilon e^{-\frac{\varepsilon}{kT}} \, d\varepsilon \tag{36}$$

$$= \frac{2}{\pi^2} \left(\frac{\pi}{kT} \right)^{\frac{3}{2}} \int_0^\infty \epsilon^{\frac{3}{2}} e^{-\frac{\varepsilon}{kT}} \, d\varepsilon. \tag{37}$$

In the last line, we have substituted for Z and $g(\varepsilon)$ from equations (24) and (20) respectively.

Now we need to perform the integral in equation (37). We make use of the standard result:

$$\int_0^\infty x^n \, e^{-\frac{x}{a}} \, dx = a^{n+1} \Gamma(n+1). \tag{38}$$

The gamma function $\Gamma(n+1)$ is a generalisation of the factorial function: for integer n, $\Gamma(n+1) = n!$. Using (38), we find:

$$\int_0^\infty \varepsilon^{\frac{3}{2}} \, e^{-\frac{\varepsilon}{kT}} \, d\varepsilon = (kT)^{\frac{5}{2}} \, \Gamma\!\left(\frac{5}{2} \right) = \frac{3\sqrt{\pi}}{4} \, (kT)^{\frac{5}{2}}. \tag{39}$$

Substituting this result into (37) gives immediately:

$$U = \frac{3}{2} NkT, \tag{40}$$

in agreement with equation (34).

Although we derived this expression for the energy assuming a square box, the result is valid for a box of any shape.

Maxwell-Boltzmann gas: total energy

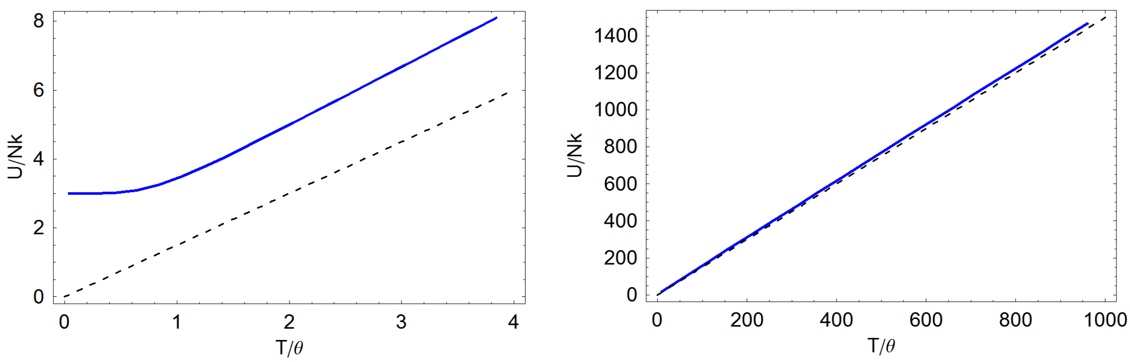
We made a high temperature approximation in order to evaluate the partition function: this limits our results to the classical regime.

However, we can evaluate numerically the exact (quantum) expressions for the partition function and for the total energy. The total energy can be written in the form:

$$U = \frac{N}{Z}\sum_j \varepsilon_j \, e^{-\frac{\varepsilon_j}{kT}} = 3Nk\theta \, \frac{\sum_{n=1}^{\infty} n^2 \, e^{-n^2\frac{\theta}{T}}}{\sum_{n=1}^{\infty} e^{-n^2\frac{\theta}{T}}}. \tag{41}$$

Let us plot the exact results, and compare with the classical limit...

Maxwell-Boltzmann gas: total energy



At low temperature $T < \theta$, we see the quantum effects as a non-zero energy of the particles in the ground state.

At high temperature, $T \gg \theta$, the energy approaches the classical limit $U = \frac{3}{2}NkT$, shown by the dashed line.

At what temperature do we expect quantum effects to become important? Let us consider 1 mm^3 of helium gas. Using:

$$\begin{aligned} m &= 6.69 \times 10^{-27}\,\text{kg}, \\ L &= 0.001\,\text{m}, \\ \hbar &= 1.05 \times 10^{-34}\,\text{Js}, \\ k &= 1.38 \times 10^{-23}\,\text{J/K}, \end{aligned}$$

we find:

$$\theta = \frac{\hbar^2 \pi^2}{2mkL^2} = 5.9 \times 10^{-13}\ \text{K}. \qquad (42)$$

This is an extremely low temperature, by anybody's standards. For all practical purposes, the classical theory should describe the behaviour of the gas very well.

From the expression (34) for the total energy of the gas:

$$U = \frac{3}{2}NkT,$$

it is trivial to find the heat capacity (for $T \gg \theta$):

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}Nk. \qquad (43)$$

The heat capacity at constant volume is constant. Note that in this case, it is important to apply the condition of constant volume, because the energy levels depend on the volume of the box.

We should remember that these results are valid only in the high temperature limit. In this limit, the energy levels are close together compared to the typical energy of a particle (of order kT), so the gas behaves like a classical system.

Using the classical approximation for the partition function Z (24):

$$Z = \left(\frac{\pi T}{4\theta}\right)^{\frac{3}{2}} \tag{44}$$

we can find an expression for the Helmholtz free energy:

$$F = -NkT \ln(Z), \tag{45}$$

and then find an expression for the entropy of the Maxwell-Botlzmann gas, using:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V . \tag{46}$$

Using (24) we can write for the Helmholtz free energy:

$$F = -NkT \ln(Z) = -\frac{3}{2}NkT \ln\left(\frac{\pi}{4}\right) - \frac{3}{2}NkT \ln\left(\frac{T}{\theta}\right). \tag{47}$$

Differentiating with respect to T, we find that the entropy is given by:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{3}{2}Nk\left[1 + \ln\left(\frac{\pi}{4}\right)\right] + \frac{3}{2}Nk \ln\left(\frac{T}{\theta}\right). \tag{48}$$

Again, this is an expression valid in the classical limit, $T \gg \theta$; and, as for the case of the collection of harmonic oscillators, it has the form:

$$S = S_0 + C_V \ln\left(\frac{T}{T_0}\right) \tag{49}$$

that we expect from classical thermodynamics, for a system with constant heat capacity at constant volume.

Also note that, as in the case of the harmonic oscillators, the expression for the entropy includes Planck's constant, even in the classical limit. Entropy is inherently a quantum phenomenon.

Comment: for an alternative discussion, using Boltzmann's equation $S = k \ln \Omega$, see Guénault (second edition) page 69.

Maxwell-Boltzmann gas: further properties

We can explore further properties of the Maxwell-Boltzmann gas. To complete our analysis of the monatomic gas, we shall calculate:

- the pressure of the gas, and its relationship to temperature and volume;
- the energy distribution of particles within the gas;
- the velocity distribution of particles within the gas.

Pressure is a thermodynamic function, used in the description of macroscopic systems. We can derive the pressure from the Helmholtz free energy, in a similar way to the derivation of the entropy.

Since the Helmholtz free energy F is given by:

$$F = U - TS, \tag{50}$$

we can use the first law of thermondynamics in the form:

$$dU = T\,dS - p\,dV, \tag{51}$$

to find that:

$$dF = -S\,dT - p\,dV. \tag{52}$$

Hence, by considering a change in volume at constant temperature, we find:

$$p = -\left(\frac{\partial F}{\partial V}\right)_T. \tag{53}$$

Now we use:

$$F = -NkT\ln(Z). \tag{54}$$

For a monatomic Maxwell-Boltzmann gas, the partition function Z is given (in the classical limit) by (24):

$$Z = \left(\frac{\pi T}{4\theta}\right)^{\frac{3}{2}}. \tag{55}$$

Using (11):

$$\theta = \frac{\hbar^2\pi^2}{2mkL^2}, \tag{56}$$

we can write:

$$Z = \left(\frac{mkTL^2}{2\pi\hbar^2}\right)^{\frac{3}{2}} = \frac{V}{V_0}, \tag{57}$$

where:

$$V = L^3 \quad \text{and} \quad V_0 = \left(\frac{2\pi\hbar^2}{mkT}\right)^{\frac{3}{2}}. \tag{58}$$

Since we have:

$$Z = \frac{V}{V_0}, \tag{59}$$

we find:

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = NkT \left(\frac{\partial \ln(Z)}{\partial V}\right)_T = \frac{NkT}{V}. \tag{60}$$

Thus, the pressure, volume and temperature for a monatomic Maxwell-Boltzmann gas are related by:

$$pV = NkT. \tag{61}$$

The equation of state (61) for a monatomic Maxwell-Boltzmann gas:

$$pV = NkT,$$

corresponds to the ideal gas equation:

$$pV = nRT. \tag{62}$$

Hence, a monatomic Maxwell-Boltzmann gas behaves (in the classical limit of high temperature) as an ideal gas.

Furthermore, since N is the number of particles in the gas, and n the number of moles, $N/n = A$, where A is Avogadro's constant. Thus, we have a relationship between Boltzmann's constant k, and the gas constant R:

$$R = kA. \tag{63}$$

Previously, we found the density of states in a Maxwell-Boltzmann gas (20) as a function of energy:

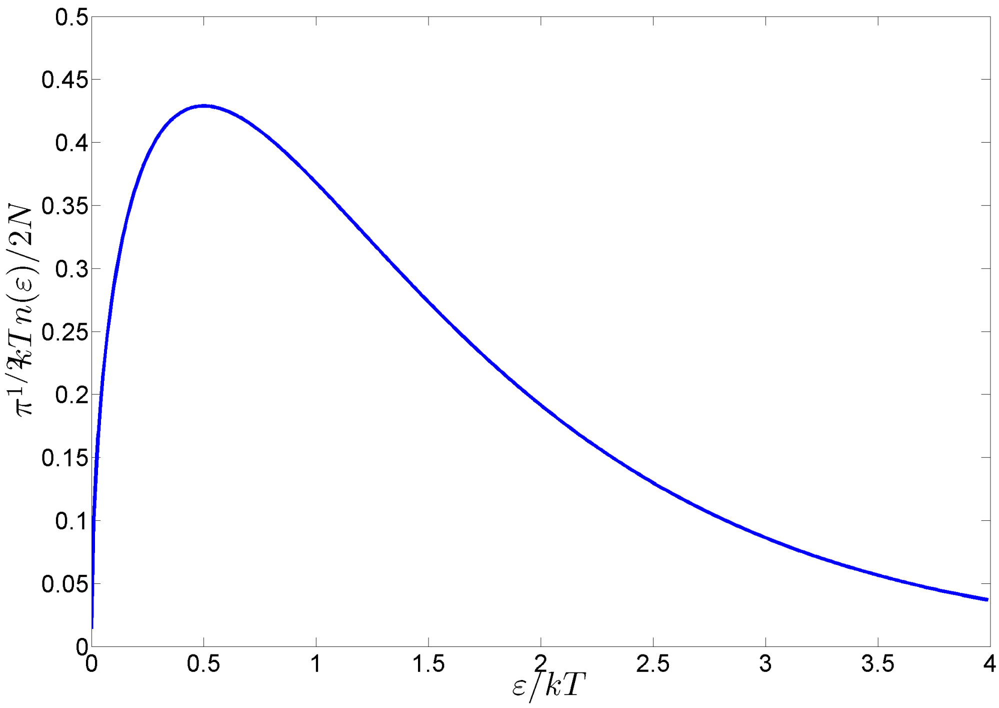
$$g(\varepsilon)\,d\varepsilon = \frac{\pi}{4}\sqrt{\frac{\varepsilon}{(k\theta)^3}}\,d\varepsilon, \tag{64}$$

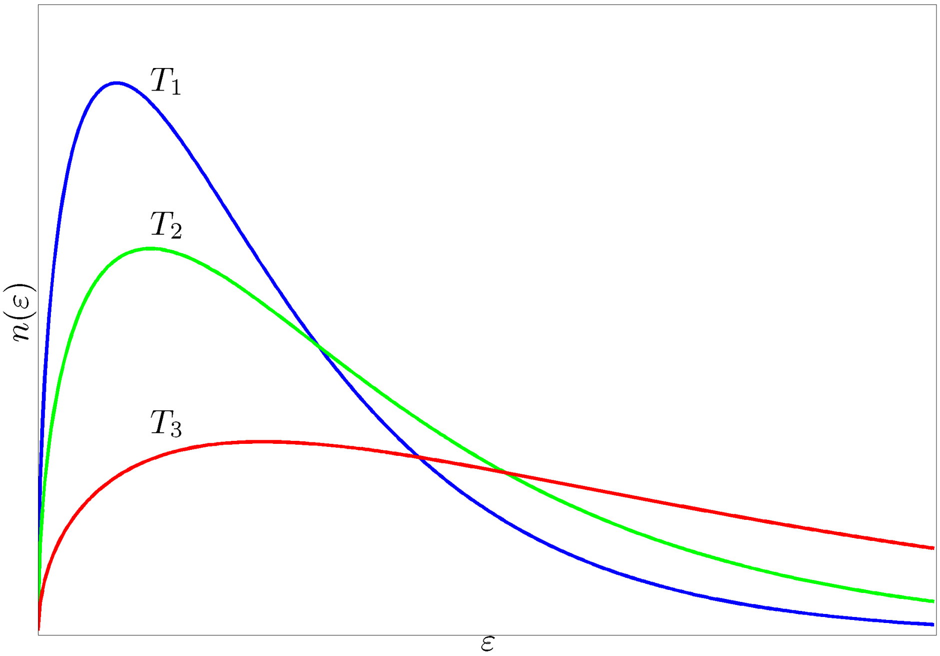
We also have the partition function, Z (24):

$$Z = \left(\frac{\pi}{4}\frac{T}{\theta}\right)^{\frac{3}{2}}. \tag{65}$$

Hence, using the Boltzmann distribution, the number of particles $n(\varepsilon)\,d\varepsilon$ in the energy range ε to $\varepsilon + d\varepsilon$ is:

$$n(\varepsilon)\,d\varepsilon = \frac{N}{Z}g(\varepsilon)e^{-\frac{\varepsilon}{kT}}\,d\varepsilon = 2\pi N\sqrt{\frac{\varepsilon}{(\pi kT)^3}}\,e^{-\frac{\varepsilon}{kT}}\,d\varepsilon. \tag{66}$$





The peak in the distribution occurs at:

$$\frac{dn(\varepsilon)}{d\varepsilon} = 0, \tag{67}$$

which we find gives:

$$\varepsilon = \frac{1}{2}kT. \tag{68}$$

The average energy over all particles is given by:

$$\bar{\varepsilon} = \frac{1}{N}\int_0^\infty \varepsilon n(\varepsilon)\, d\varepsilon. \tag{69}$$

We have, of course, evaluated this integral before, when calculating the total energy. The result, using equation (38), is:

$$\bar{\varepsilon} = \frac{3}{2}kT. \tag{70}$$

Finally, we turn to the velocity distribution of particles in a monatomic Maxwell-Boltzmann gas. We can obtain this directly from the energy distribution, by substituting:

$$\varepsilon = \frac{1}{2} m v^2, \tag{71}$$

and:

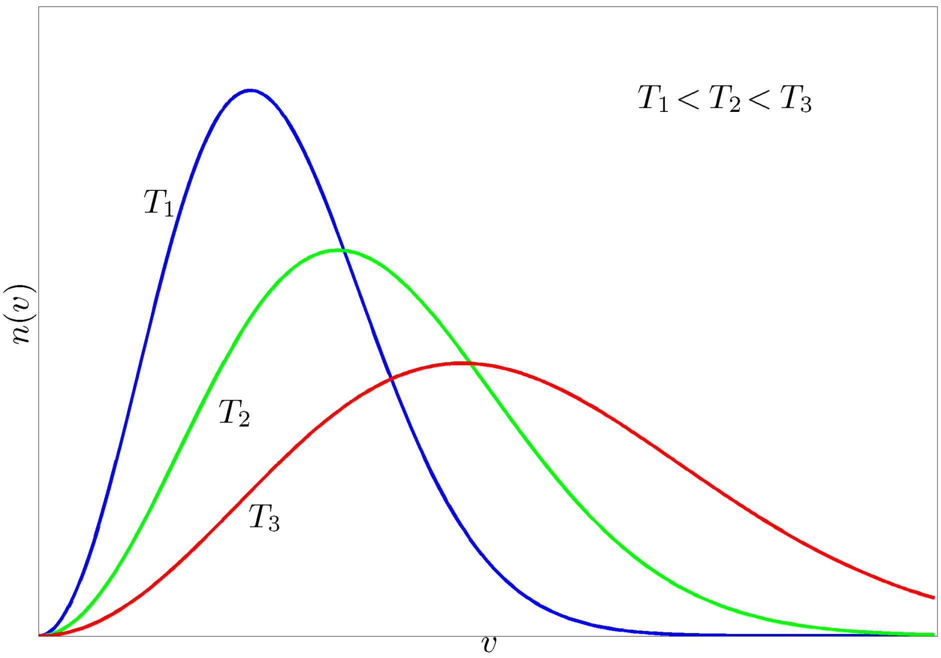
$$d\varepsilon = m v \, dv \tag{72}$$

into equation (66).

The resulting expression for the energy distribution is:

$$n(v)\, dv = 4\pi N \left(\frac{m}{2\pi k T} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}} \, dv. \tag{73}$$

The velocity distribution $n(v)$ is known as the Maxwell-Boltzmann distribution.



The most probable velocity for a particle in the gas is the velocity at which the velocity distribution peaks. This is found by solving:

$$\frac{dn}{dv} = 0. \tag{74}$$

Since:

$$n(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 \, e^{-\frac{mv^2}{2kT}}, \tag{75}$$

we find:

$$\frac{dn}{dv} = 0 \quad \text{when} \quad v = \hat{v} = \sqrt{\frac{2kT}{m}}. \tag{76}$$

The mean velocity of particles in a Maxwell-Boltzmann gas is given by:

$$\bar{v} = \frac{1}{N}\int_0^\infty v \, n(v) \, dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^\infty v^3 \, e^{-\frac{mv^2}{2kT}} \, dv. \tag{77}$$

The integral is the third Maxwell-Boltzmann integral, I_3 (see Appendix A). It is evaluated using:

$$I_3 = \int_0^\infty x^3 \, e^{-bx^2} \, dx = \frac{1}{b} I_1 = \frac{1}{2b^2}. \tag{78}$$

Hence, putting $b = m/2kT$, we find:

$$\bar{v} = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \frac{1}{2} \left(\frac{2kT}{m}\right)^2 = \sqrt{\frac{8kT}{\pi m}}. \tag{79}$$

The mean square velocity of particles in a Maxwell-Boltzmann gas is given by:

$$\overline{v^2} = \frac{1}{N} \int_0^\infty v^2 \, n(v) \, dv = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \int_0^\infty v^4 \, e^{-\frac{mv^2}{2kT}} \, dv. \tag{80}$$

The integral is the fourth Maxwell-Boltzmann integral, I_4 (see Appendix A). It is evaluated using:

$$I_4 = \int_0^\infty x^4 \, e^{-bx^2} \, dx = \frac{3}{2b} I_2, \tag{81}$$

and:

$$I_2 = \int_0^\infty x^2 \, e^{-bx^2} \, dx = \frac{1}{2b} I_0 = \frac{1}{4b} \sqrt{\frac{\pi}{b}}. \tag{82}$$

Hence,

$$I_4 = \frac{3}{8b^2} \sqrt{\frac{\pi}{b}}, \tag{83}$$

Thus, putting $b = m/2kT$, we find:

$$\overline{v^2} = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \frac{3\sqrt{\pi}}{8} \left(\frac{2kT}{m} \right)^{\frac{5}{2}} = \frac{3kT}{m}. \tag{84}$$

Note that this implies that the mean kinetic energy of a particle in the gas is:

$$\bar{\varepsilon} = \frac{1}{2} m \overline{v^2} = \frac{3}{2} kT, \tag{85}$$

which is consistent with our result for the total energy of the gas (34):

$$U = \frac{3}{2} NkT. \tag{86}$$

In terms of the parameter:

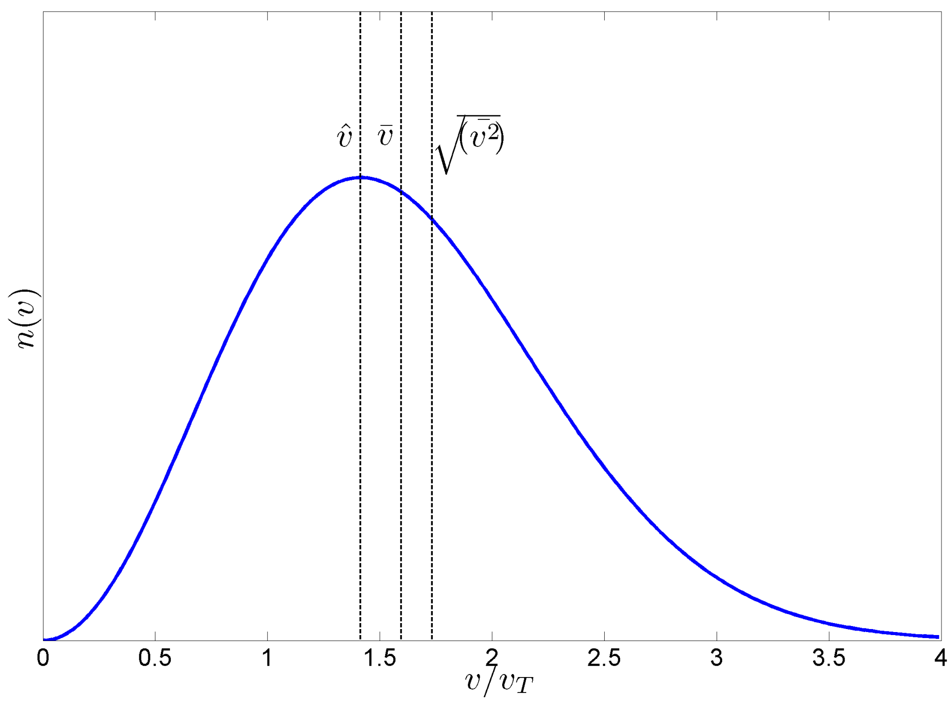
$$v_T = \sqrt{\frac{kT}{m}} \tag{87}$$

the most probable velocity $\hat{v}$, mean velocity $\bar{v}$ and root mean square velocity $\sqrt{\overline{v^2}}$ are given by:

$$\hat{v} = \sqrt{2}v_T, \tag{88}$$

$$\bar{v} = \sqrt{\frac{8}{\pi}}v_T, \tag{89}$$

$$\sqrt{\overline{v^2}} = \sqrt{3}v_T. \tag{90}$$



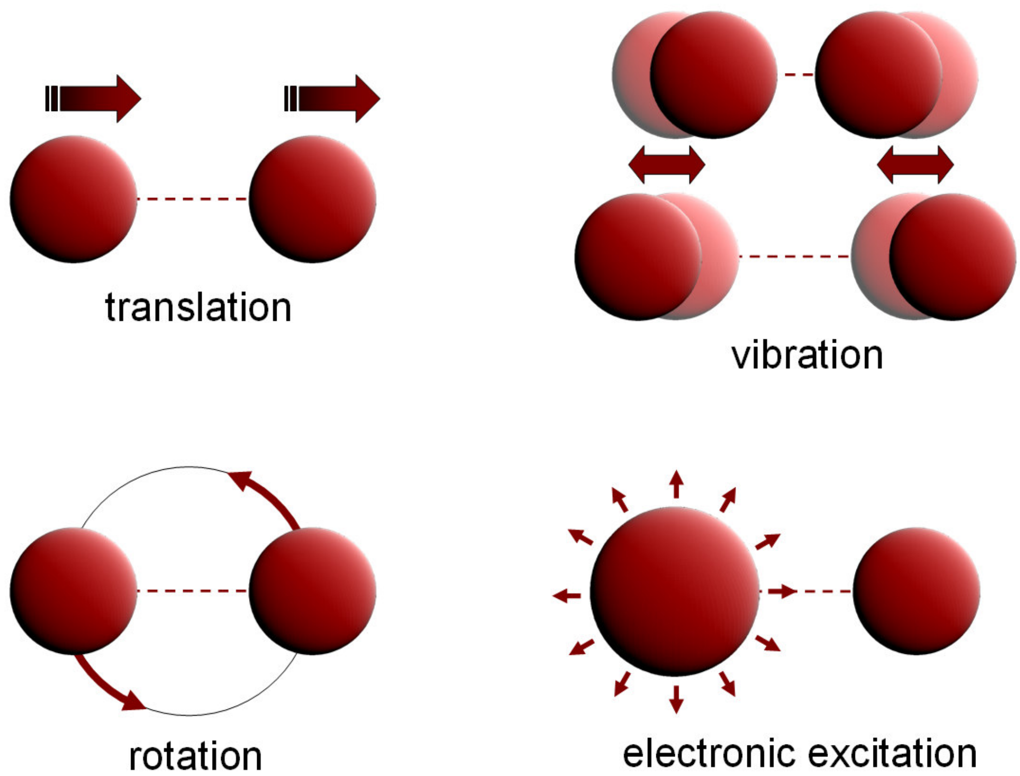
Diatomic Maxwell-Boltzmann gas

So far, we have assumed that the particles in the gas have no internal structure. In other words, the only kind of energy they can possess is the "translational" kinetic energy associated with their velocity as they move through the box.

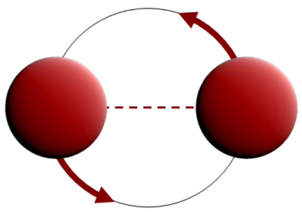
This is a real model for monatomic gases: but there are only a few examples of such gases. Most gases are composed of molecules consisting of two or more atoms.

The internal structure in a diatomic molecule provides additional energy states for the molecule. These energy states are associated with rotation and vibration of the molecule. We also now include the possibility of electronic excitation of one or both of the atoms in the molecule.

Diatomic molecule degrees of freedom

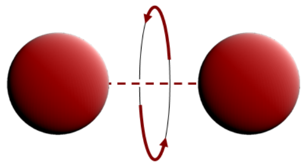


Note that rotational energy states only include those with *orbital* angular momentum, in which the positions of the atoms change with time. Generally, the intrinsic angular momentum associated with the *spin* of the atoms is fixed.



Orbital angular momentum.

Energy levels: $\varepsilon_l = \frac{\hbar^2}{2I} l(l+1)$.



Spin angular momentum.
Fixed energy.

We must modify our theory to take into account the extra energy levels associated with rotations, vibrations, and electronic excitation. To keep things simple, we will assume that the degrees of freedom are independent of each other. That is, the vibration of the atoms within a molecule does not affect the rotational energy, and vice-versa.

In practice, this is not exactly true, but is a good approximation. It allows us to write the total energy of a particle in the gas as a simple sum of the energies associated with the various degrees of freedom:

$$\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rotn}} + \varepsilon_{\text{vibn}} + \varepsilon_{\text{elec}}. \tag{91}$$

The partition function Z then becomes:

$$Z = \sum \exp\left(-\frac{\varepsilon}{kT}\right) = \sum \exp\left(-\frac{1}{kT}\left(\varepsilon_{\mathrm{t}} + \varepsilon_{\mathrm{r}} + \varepsilon_{\mathrm{v}} + \varepsilon_{\mathrm{e}}\right)\right). \quad (92)$$

The summations extend over all possible states.

The partition function can now be expressed as:

$$Z = \sum e^{-\frac{\varepsilon_{\mathrm{t}}}{kT}} \cdot \sum e^{-\frac{\varepsilon_{\mathrm{r}}}{kT}} \cdot \sum e^{-\frac{\varepsilon_{\mathrm{v}}}{kT}} \cdot \sum e^{-\frac{\varepsilon_{\mathrm{e}}}{kT}}. \quad (93)$$

Hence, the partition function can be written as a product of partition functions associated with each of the degrees of freedom:

$$Z = Z_{\mathrm{trans}} \cdot Z_{\mathrm{rotn}} \cdot Z_{\mathrm{vibn}} \cdot Z_{\mathrm{elec}}. \quad (94)$$

Recall that the energy and the entropy depend on the logarithm of the partition function:

$$U = N\frac{d \ln Z}{d\beta}, \qquad \beta = -\frac{1}{kT}; \quad (95)$$

and:

$$S = -\left(\frac{dF}{dT}\right)_V, \qquad F = -NkT \ln Z. \quad (96)$$

Since Z is the product of partition functions associated with each of the degrees of freedom, the logarithm of Z becomes a sum of the logarithms of the different partition functions:

$$\ln Z = \ln Z_{\mathrm{t}} + \ln Z_{\mathrm{r}} + \ln Z_{\mathrm{v}} + \ln Z_{\mathrm{e}}. \quad (97)$$

This is very convenient. It means that the total energy, the entropy, and the heat capacity are simply sums of contributions from the different degrees of freedom.

The heat capacity is something that is easy to measure directly in the laboratory; so we shall focus our attention on this. Our aim is to calculate the total heat capacity of a diatomic gas, taking into account all the degrees of freedom of the particles.

Let us consider the contribution to the heat capacity of each of the degrees of freedom in turn, starting with the translational energy. This is very easy: everything is the same as in the case of the monatomic gas.

The contribution to the heat capacity from the translational energy is:

$$C_V^{(\mathrm{t})} = \frac{3}{2}Nk. \tag{98}$$

Remember that this is valid in the classical regime, which is appropriate for all gases under ordinary conditions.

Next, let us consider the electronic excitation. Typically, the first excited state will have an energy that is of order 10 eV above the ground state. The population of the first excited state, relative to the ground state, will be:

$$\frac{e^{-\frac{\varepsilon_1}{kT}}}{e^{-\frac{\varepsilon_0}{kT}}} = e^{-\frac{\varepsilon_1 - \varepsilon_0}{kT}}, \tag{99}$$

where $\varepsilon_1 - \varepsilon_0 \approx 10$ eV. At room temperature, $T \approx 290$ K, and $kT \approx 0.025$ eV. Hence, the first excited state has a population of approximately $e^{-400} \approx 0$ relative to the ground state.

At ordinary temperatures, the electrons in all the atoms will be in the ground state: we expect electronic excitation to make *no* contribution to the heat capacity of the gas.

Now let us consider the vibrational motion. For this degree of freedom, we can treat the diatomic molecule as a quantum harmonic oscillator, with energy levels:

$$\epsilon_j = j\hbar\omega, \tag{100}$$

where ω is determined by the strength of the bond between the atoms, and the mass of the atoms.

We define a parameter θ_v, with units of temperature, such that:

$$k\theta_\mathrm{v} = \hbar\omega. \tag{101}$$

From Part 2 of this course, where we considered a collection of quantum harmonic oscillators, we can then write for the vibrational contribution to the heat capacity:

$$C_V^{(\mathrm{v})} = \frac{Nk\left(\frac{\theta_\mathrm{v}}{T}\right)^2 e^{\frac{\theta_\mathrm{v}}{T}}}{\left(e^{\frac{\theta_\mathrm{v}}{T}} - 1\right)^2}. \tag{102}$$

Studying the behaviour of the heat capacity is one way to determine the value of the parameter θ_v for particular gases: this will become clear shortly, when we sum the contributions to the heat capacity from the various degrees of freedom. For now, we simply note that for many gases, the value of θ_v is of order of a few thousand kelvin:

Gas	θ_v
O_2	2000 K
N_2	3000 K
H_2	6000 K

Recall that for $T \ll \theta_\mathrm{v}$, the first excited energy level of the oscillator is significantly above the energy kT; hence, at room temperature where $T \approx 290$ K, the molecules of most diatomic gases will be in their ground vibrational state. At room temperature, the vibrational degree of freedom makes little contribution to the heat capacity.

For $T \gg \theta_\mathsf{v}$, the heat capacity of a collection of quantum oscillators approaches the value Nk. However, at a few thousand kelvin, the molecules of many gases start to dissociate into individual atoms. This means that the vibrational degree of freedom only makes a contribution to the heat capacity over a relatively small range of temperature.

Finally, let us consider the rotational degree of freedom. From quantum theory, we know that the energy levels of a system with orbital angular momentum are given by:

$$\varepsilon_\ell = \frac{\hbar^2}{2I}\ell(\ell+1), \tag{103}$$

where ℓ is a positive integer ($\ell = 1, 2, 3...$), and I is the moment of inertia.

We also know that within each energy level, there are $g = (2\ell+1)$ distinct states (in other words, the energy levels have a degeneracy $2\ell+1$.) Thus, the partition function can be written:

$$Z_\mathsf{r} = \sum_\ell g\, e^{-\frac{\varepsilon_\ell}{kT}} = \sum_\ell (2\ell+1)\, e^{-\ell(\ell+1)\frac{\theta_\mathsf{r}}{T}}. \tag{104}$$

where we define the parameter θ_r (with units of temperature) such that:

$$k\theta_\mathsf{r} = \frac{\hbar^2}{2I}. \tag{105}$$

As usual, the parameter θ_{r} characterises the temperature at which the degree of freedom starts to make a contribution to the heat capacity. It depends on the moment of inertia of the molecule: this may be estimated from a classical model, if the masses m_1 and m_2 and distance $2r$ between the atoms are known:

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2. \tag{106}$$

Or, θ_r may be obtained from experiment. We will not go into the details, but simply quote some results:

Gas	θ_{r}
O_2	2.1 K
N_2	2.9 K
H_2	85 K
HD	64 K

The values of θ_{r} are very low: typically (except for hydrogen) below the boiling point of the gas. This is a consequence of the fact that rotational energies are quite low, certainly compared to vibrational energies. Typically, the rotational degree of freedom will always contribute to the energy of a gas, and hence to the heat capacity.

Since at room temperature, most gases have $T \gg \theta_{\mathrm{r}}$, a gas at room temperature will be in a classical regime for the rotational energy, where the difference between energy levels is small compared to the typical rotational energy of a molecule. In other words, we can treat the energy levels as a continuum. This is fortunate, since otherwise it would be very hard to do the summation in the partition function...

Making a classical approximation, we can write the partition function for the rotational degree of freedom (104):

$$Z_{\mathrm{r}} = \sum_{\ell} (2\ell + 1)\, e^{-\ell(\ell+1)\frac{\theta_{\mathrm{r}}}{T}} \approx \int_0^\infty (2\ell + 1)\, e^{-\ell(\ell+1)\frac{\theta_{\mathrm{r}}}{T}}\, d\ell. \qquad (107)$$

The integral is easier than it looks. We define a new variable y:

$$y = \ell(\ell + 1) \qquad \therefore \qquad dy = (2\ell + 1)\, d\ell. \qquad (108)$$

Then the integral becomes:

$$Z_{\mathrm{r}} \approx \int_0^\infty e^{-y\frac{\theta_{\mathrm{r}}}{T}}\, dy = \frac{T}{\theta_{\mathrm{r}}}. \qquad (109)$$

Now that we have the partition function (in the classical limit), we can find the total energy U_{r} associated with the rotational degree of freedom. This is given by:

$$U_{\mathrm{r}} = N\frac{d \ln Z_{\mathrm{r}}}{d\beta}, \qquad \beta = -\frac{1}{kT}. \qquad (110)$$

Using $Z_{\mathrm{r}} = \frac{T}{\theta_{\mathrm{r}}}$ we find:

$$U_{\mathrm{r}} = NkT, \qquad (111)$$

and hence the heat capacity is given by:

$$C_V^{(\mathrm{r})} = Nk. \qquad (112)$$

It is important to remember that this expression is valid in the classical limit, $T \gg \theta_{\mathrm{r}}$. For $T \ll \theta_{\mathrm{r}}$, the rotational degree of freedom will not be excited, and the total energy and the heat capacity will be zero.

In summary, we expect the heat capacity of a diatomic gas to vary with temperature as follows:

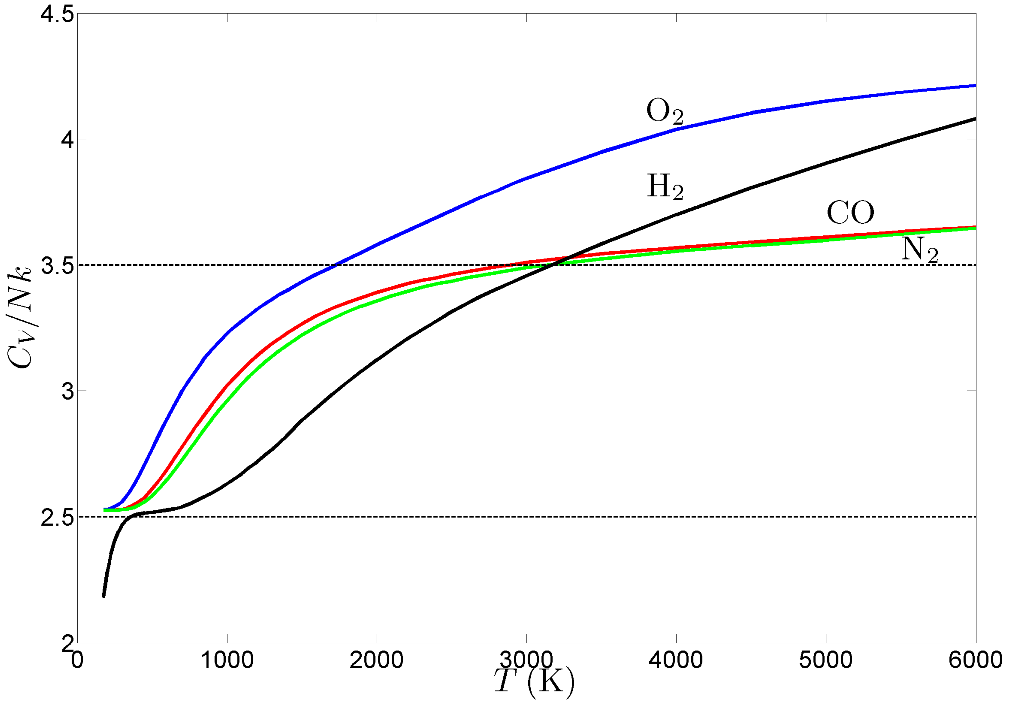
T range	$C_V^{(\mathrm{t})}$	$C_V^{(\mathrm{r})}$	$C_V^{(\mathrm{v})}$	Total C_V
$\theta < T < \theta_\mathrm{r}$	$\frac{3}{2}Nk$	0	0	$\frac{3}{2}Nk$
$\theta_\mathrm{r} < T < \theta_\mathrm{v}$	$\frac{3}{2}Nk$	Nk	0	$\frac{5}{2}Nk$
$\theta_\mathrm{v} < T$	$\frac{3}{2}Nk$	Nk	Nk	$\frac{7}{2}Nk$

Recall that:

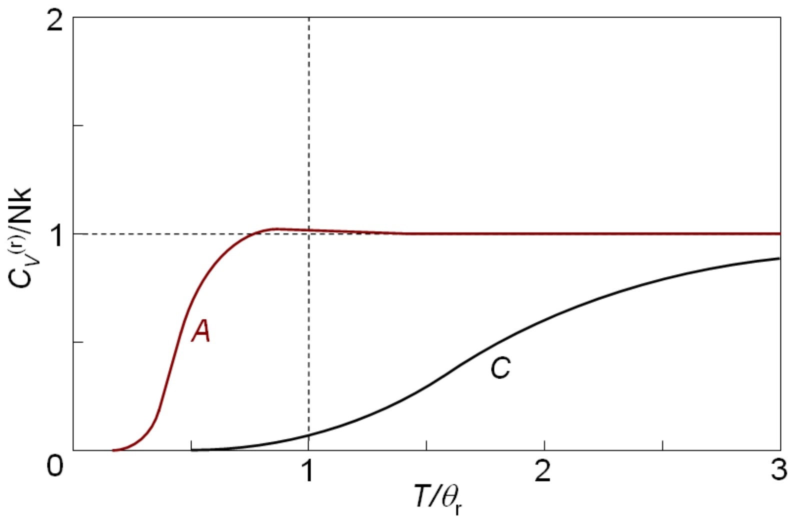
$$\theta = \frac{\hbar^2\pi^2}{2mkV^{\frac{2}{3}}}, \quad \theta_\mathrm{r} = \frac{\hbar^2}{2Ik}, \quad \theta_\mathrm{v} = \frac{\hbar\omega}{k}, \tag{113}$$

where V is the volume of the container; I the moment of inertia of a gas molecule; and ω the frequency of vibration of the atoms in the molecule.

For real gases, the theory appears to work reasonably well...



A closer look at the heat capacity of hydrogen suggests that there may be a problem. A careful calculation suggests that, for the rotational heat capacity $C_V^{(\mathrm{r})}$, we should find curve A in the figure below; in fact, experimentally, curve C is found.



The reason for the discrepancy is to do with the spins of the nuclei of the atoms in a hydrogen molecule. The nucleus of a hydrogen atom is a proton, which has spin-$\frac{1}{2}$. For a hydrogen molecule, the spins can be parallel, in which case they sum to spin-1 (ortho-hydrogen); or the spins can be antiparallel, in which case they sum to spin-0 (para-hydrogen).

The spin-1 states have an additional three-fold degeneracy compared to the spin-0 states. We need to take this into account when finding the partition function.

In a hydrogen molecule, the total spin and the orbital angular momentum of the protons couple in an interesting way. Because protons are fermions, the wave function of the system must be *antisymmetric* under interchange of the coordinates of the two protons, i.e.

$$\psi(x_1, x_2) = -\psi(x_2, x_1). \tag{114}$$

A state with orbital angular momentum ℓ is symmetric under interchange of the protons if ℓ is even, and antisymmetric if ℓ is odd. The state with spin-0 (spins of the two protons antiparallel) is antisymmetric; while the three states with spin-1 (spins parallel) are symmetric.

Thus, the possible combinations of spin and orbital angular momentum are:

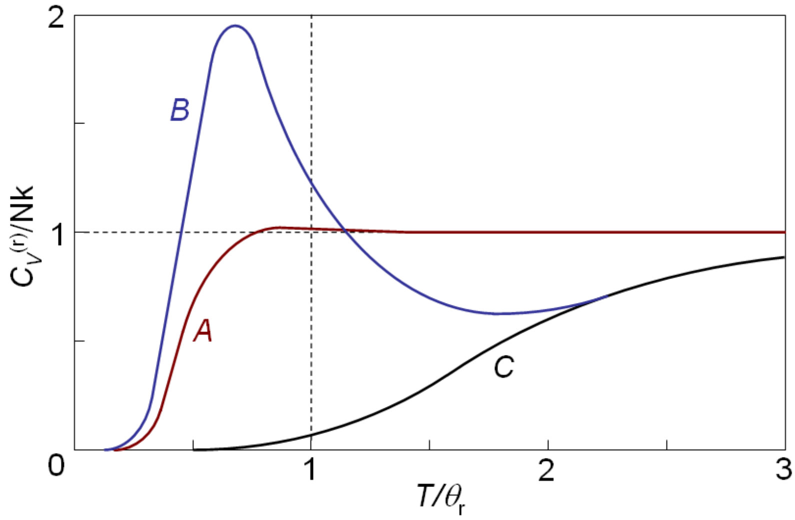
- ℓ even; spin-0 (single spin state for each ℓ);
- ℓ odd; spin-1 (three spin states for each ℓ).

Taking into account the additional degeneracy associated with the spins of the hydrogen nuclei, the partition function for the rotational degree of freedom should become:

$$Z_\mathrm{r} = \sum_{\ell\ \mathrm{even}} (2\ell + 1) e^{-\ell(\ell+1)\frac{\theta_\mathrm{r}}{T}} + 3 \sum_{\ell\ \mathrm{odd}} (2\ell + 1) e^{-\ell(\ell+1)\frac{\theta_\mathrm{r}}{T}}. \tag{115}$$

If we compute the rotational heat capacity using this new partition function...

...we get curve B in the plot. There is an even great discrepancy with the experimental results, curve C!



The reason for the discrepancy is that in hydrogen gas, the probability for a molecule to change from ortho-hydrogen to para-hydrogen (or vice-versa) in a collision with another molecule is extremely low. Molecules tend to stay in their spin states. If we take that into account, then we should treat the two components as different gases, each with their own rotational heat capacity, derived from the two distinct summations in the partition function (115).

If ortho-hydrogen has three-times greater concentration in a sample than para-hydrogen (as may be assumed from there being three times as many possible states for any given rotational energy), then the total heat capacity will be:

$$C_V^{(\mathrm{r})} = \frac{3}{4} C_{V,ortho}^{(\mathrm{r})} + \frac{1}{4} C_{V,para}^{(\mathrm{r})}. \qquad (116)$$

This heat capacity gives the curve C in the previous figure... in agreement with experiment, at last!

Finally, we mention that if the measurement of the heat capacity is done slowly, or in the presence of a catalyst that increases the rate of conversion between the ortho- and para-states, then curve B in the previous figure is indeed obtained experimentally. This is because the system is able to achieve an equilibrium between the states, in which case the assumptions leading to the partition function (115) are satisfied.

It is worth noting that the strange behaviour of the heat capacity of hydrogen really is a consequence of the fact that the atomic nuclei are idential fermions. A gas consisting of molecules of HD (an atom of hydrogen bound to an atom of deuterium) shows none of the strange behaviour of H_2; the variation of heat capacity of HD with temperature is similar to other diatomic gases.

Summary

You should be able to:

- Explain what is meant by a Maxwell-Boltzmann gas.
- Derive expressions for the density of states and the partition function in a Maxwell-Boltzmann gas, in the classical limit.
- Explain and check in particular cases the low-density condition for a Maxwell-Boltzmann gas.
- Derive, as functions of temperature, the energy; heat capacity; entropy; and pressure of a Maxwell-Boltzmann gas.
- Derive the energy and velocity distributions, as functions of temperature, for a Maxwell-Boltzmann gas.
- Calculate the most probable velocity, mean velocity, and mean square velocity of particles in a Maxwell-Boltzmann gas.
- Describe the additional degrees of freedom in a diatomic gas compared to a monatomic gas, and explain how they contribute to the partition function, and to the heat capacity.
- Give a qualitative description of the behaviour of the rotational heat capacity of hydrogen as a function of temperature, and explain this behaviour in terms of the ortho and para states of hydrogen molecules.

To find the mean velocity and mean square velocity of particles in a Maxwell-Boltzmann gas, we need to evaluate integrals of the form:

$$I_n = \int_0^\infty x^n \, e^{-bx^2} \, dx. \tag{117}$$

The case $n = 0$ is the standard Gaussian integral:

$$I_0 = \int_0^\infty e^{-bx^2} \, dx = \frac{1}{2}\sqrt{\frac{\pi}{b}}. \tag{118}$$

For $n = 1$, the integrand $x \, e^{-bx^2}$ is the derivative of $-e^{-bx^2}/2b$, and so:

$$I_1 = \int_0^\infty x \, e^{-bx^2} \, dx = \left[-\frac{e^{-bx^2}}{2b} \right]_0^\infty = \frac{1}{2b}. \tag{119}$$

Other integrals in the series may be found from a recursion formula, which is obtained by integrating by parts...

Integrating by parts gives:

$$I_n = \int_0^\infty x^n \, e^{-bx^2} \, dx = \left[\frac{x^{n+1}}{n+1} \, e^{-bx^2} \right]_0^\infty - \int_0^\infty \frac{x^{n+1}}{n+1} \, (-2bx) e^{-bx^2} \, dx. \tag{120}$$

Hence we find:

$$I_n = \int_0^\infty \frac{2b}{n+1} \, x^{n+2} e^{-bx^2} \, dx = \frac{2b}{n+1} \, I_{n+2}. \tag{121}$$

This may be written as:

$$I_{n+2} = \frac{n+1}{2b} \, I_n, \tag{122}$$

or, substituting $n-2$ for n:

$$I_n = \frac{n-1}{2b} \, I_{n-2}. \tag{123}$$